

Electrooxidation of methanol on Pt–Ru catalysts supported by basal plane graphite in phosphoric acid solution

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Abstract

The electrooxidation of methanol on Pt–Ru catalyst supported by basal plane graphite was investigated in phosphoric acid solution by cyclic voltammetry, X-ray diffraction (XRD) and scanning electron microscope (SEM). Pt–Ru catalysts were prepared by applying a potential of 0.0 V in chloroplatinic acid solution of various ruthenium chloride concentrations. The peak potential of methanol oxidation is shifted to a lower potential as the concentration ratio of Ru/Pt in the electrodeposition solution. Shifts of peak potential are due to the difference of the oxidation pathway of CO adsorbed on the surface of Pt–Ru catalyst. For methanol oxidation in phosphoric acid solution, the electrocatalytic activity of the catalyst prepared in ruthenium chloride solutions of chloroplatinic acid solution (1:1) was better than that of catalysts prepared in different concentrations of ruthenium chloride solution. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The direct methanol fuel cell (DMFC) using a polymer electrolyte membrane is a promising candidate for the application of portable power sources, electric vehicles and transport applications because it does not require any fuel processing equipment. However, a challenging problem in the development of a DMFC is to find an electrocatalyst that can effectively enhance the electrode kinetics of methanol oxidation [1–3]. In addition, electrolyte selection will be an important factor as will operating conditions. Phosphoric acid electrolytes can be used at high temperature and the poisoning effect on the catalyst by anions will be less than for other electrolytes (e.g., HCl, KCl) [4,5].

On the other hand, the oxidation of methanol on the surface of platinum based electrocatalysts is accepted to be as follows:



It is known that methanol is easily oxidized on the surface of platinum catalysts to produce intermediates such

as formic acid, formaldehyde and carbon monoxide (CO). The CO among these intermediates is adsorbed on to Pt surface and diminishes electrocatalytic activity. It is known as the poisoning effect. Secondary metals such as Ru, WO₃ or Sn, were used to decrease the poisoning effect [1,2,6]. Oxidation of adsorbed CO to CO₂ requires the co-adsorption of an oxygen containing species (e.g., OH, H₂O). It is known that ruthenium forms surface oxides in the potential range of methanol oxidation [3].

Wang [6] reported that factors influencing the oxidation of carbon monoxide include the type and composition of the catalyst. Moreover, it is known that in the oxidation of methanol, the concentration of electrolyte [7,8], of methanol, and the temperature influence the peak potential and current.

The objective of this work was to prepare Pt–Ru catalysts in 20 mM chloroplatinic acid solution containing various concentrations of ruthenium chloride by electrodeposition and to evaluate their efficiency as methanol electrocatalysts. The growth of Pt–Ru catalyst was observed by using X-ray diffraction (XRD) and scanning electron microscope (SEM). The peak potential is shifted according to increasing concentration of ruthenium chloride in the electrodeposition solution. This is discussed in terms of

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oxidation pathways of carbon monoxide adsorbed on the catalyst surface.

2. Experimental

2.1. The preparation of platinum–ruthenium catalysts

The substrate electrode, which is basal plane graphite (BPG) with a surface area of 0.28 cm^2 , was polished with an alumina (diameter $0.3 \text{ }\mu\text{m}$) water slurry, washed with copious amounts of water, and ultrasonicated in deionized water for 20 min before use.

BPG-supported Pt–Ru catalysts with a total charge of 1 C were typically prepared by applying a potential of 0.0 V in 20 mM chloroplatinic acid solution with various ruthenium chloride concentrations from 5 to 40 mM. The resultant electrode was washed with a stream of deionized water, and then dried for 30 min at 100°C under 1 Torr. Chloroplatinic acid and ruthenium chloride of reagent grade were used.

Electrodeposition is to be preferred for this purpose rather than other methods because of greater simplicity, selectivity, current efficiency and control when suitable experimental conditions have been established.

2.2. Electrochemical measurement

All electrochemical measurements were conducted in a three-electrode cell under a nitrogen atmosphere at room temperature. A saturated calomel electrode (SCE) and a Pt wire were used as reference and counter electrode, respectively. Methanol and phosphoric acid of reagent grade were used and deionized water (Milli-Q water system, Millipore) was used throughout. Quoted potentials are given with respect to the SCE.

Methanol oxidation on the Pt–Ru catalysts was investigated in phosphoric acid solution by using an M283 potentiostat/galvanostat controlled by a GPIB interfaced IBM computer.

XRD spectra were measured with an X-ray diffractometer (D/Max-RC, RIGAKU) using Cu K α radiation. The morphology of the catalyst surface was obtained by using an SEM (XL3, Phillips).

3. Results and discussion

Fig. 1 shows cyclic voltammograms obtained on Pt–Ru catalysts in 0.1 M H_3PO_4 . The peak of hydrogen desorption on Pt–Ru catalysts is presented in the range of -0.3 – 0.0 V and the reduction peak of ruthenium in range of 0.3 – -0.1 V. According to previous reports, for hydrogen adsorption and desorption [7,9–11], the peak related to hydrogen desorption disappears with an increase in the

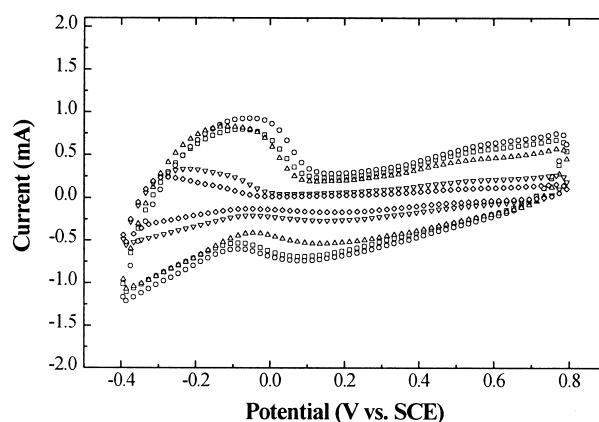


Fig. 1. Cyclic voltammograms obtained on Pt–Ru catalysts in 0.1 M H_3PO_4 with potential sweep rate of 20 mV/s. Pt–Ru catalysts were prepared in chloroplatinic acid solution of various ruthenium chloride concentrations: (\square) 5 mM; (\circ) 10 mM; (\triangle) 20 mM; (∇) 30 mM; (\diamond) 40 mM.

content of ruthenium in the Pt–Ru catalyst. For Pt–Ru catalyst prepared from 5 mM ruthenium chloride solution, for hydrogen desorption only one peak is present at 0.0 V, while two peaks for that of 30 mM are observed at 0.0 and -0.25 V, respectively. However, for Pt–Ru catalyst prepared from 40 mM ruthenium chloride solution, the peak located at 0.0 V disappears and the peak at -0.25 V is increased. This result is consistent with that observed by Chu and Gilman [7]. This suggests that the content of ruthenium in the Pt–Ru catalyst increases with increasing concentration of ruthenium chloride in the electrodeposition solution.

It is well known that the peak potential for methanol oxidation on a platinum catalyst lies at about 0.6 V and is dependent on the choice of electrolytes, acidity, and sweep rate. On the other hand, Gasteiger [10,11] argued that the rate-determining step for methanol oxidation is an adsorption step of methanol on the platinum catalyst leading to the oxidation of adsorbed carbon monoxide. According to his arguments, he indicated that in Pt-based binary catalysts, e.g., Pt–Ru, the peak potential should be constant because methanol is decomposed only on the surface of platinum catalysts at low potentials. However, this view is still contentious.

For Pt–Ru catalysts prepared in an electrodeposition solution with 50% ruthenium chloride, cyclic voltammograms in 0.1 M phosphoric acid solutions with and without methanol are shown in Fig. 2a. Peak potentials for methanol oxidation are located at 0.57 V and the peak current is 3.85 mA. It is shifted to a low potential compared with that of a Pt catalyst. Fig. 2b shows cyclic voltammograms of methanol oxidation on Pt–Ru catalysts in 0.1 M H_3PO_4 solution containing 0.1 M CH_3OH . The catalysts used were prepared by applying a potential of 0.0 V in chloroplatinic acid solution with various ruthenium chloride concentrations. The onset of methanol oxidation below 0.2

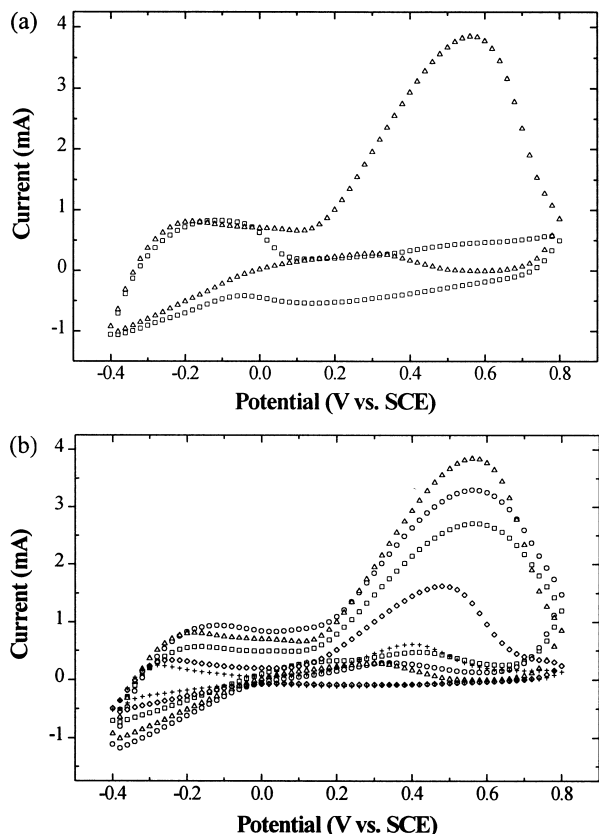


Fig. 2. Cyclic voltammograms in 0.1 M H_3PO_4 solutions with (- Δ -) and without (- \square -) 0.1 M CH_3OH (a) and Pt-Ru catalysts prepared in chloroplatinic acid solution of various ruthenium chloride concentrations (b) with potential sweep rate of 20 mV/s: (- \square -) 5 mM; (- \circ -) 10 mM; (- Δ -) 20 mM; (- \diamond -) 30 mM; (- + -) 40 mM. CVs in (a) were obtained from Pt-Ru catalyst prepared in chloroplatinic acid solution of ruthenium chloride (1:1).

V is independent of the concentration change of ruthenium in the electrodeposition solution. The peak potential for methanol oxidation is shifted to a low potential according to the increase of ruthenium chloride concentration in the electrodeposition solution as shown in Fig. 3a. It could be considered that this trend is responsible for the difference with oxidation pathway for adsorbed CO discussed below. Wang [6] reported that the peak potential for the oxidation of adsorbed CO depends on the type of catalyst used. On the other hand, when methanol is decomposed, solely on the surface of platinum catalyst particle, it produces intermediates, such as formic acid and formaldehyde; these are oxidized to carbon monoxide which then adsorb on the catalyst surface. It seems that the CO is adsorbed mainly on platinum particle surfaces, partly on ruthenium surfaces and is also dissolved in the electrolyte solution. Therefore, the pathway of adsorbed CO oxidation could be considered according to the following reactions:

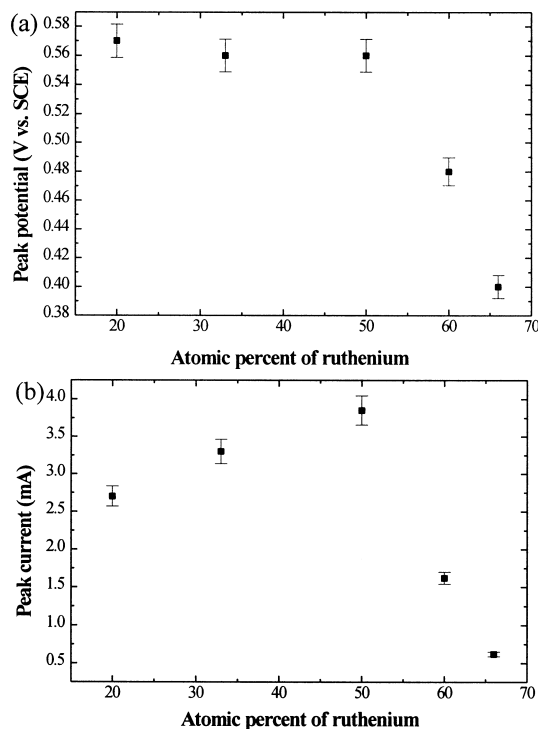
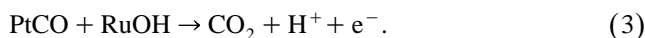
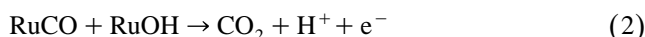
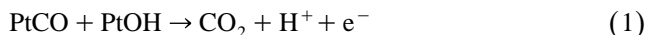


Fig. 3. Plot on peak potential (a) and current (b) vs. the atomic percent of ruthenium in electrodeposition solutions.

In the binary catalyst system, the oxidation of carbon monoxide adsorbed on the catalyst will occur via a pathway with low activation energy because of competing reactions. According to the Arrhenius equation, the rate constant increases as the activation energy decreases. Wang [6] reported that rate constant for the oxidation of CO on surface of Pt-Ru catalysts was 10^3 higher than that for pure Pt catalysts. Therefore, it could be considered that the oxidation pathway for adsorbed CO is dominated by Eqs. (2) and (3) reactions for higher ruthenium contents in the Pt-Ru catalyst, while it is dominated by Eq. (1) as the content of ruthenium decreases. Fig. 3b plots peak current

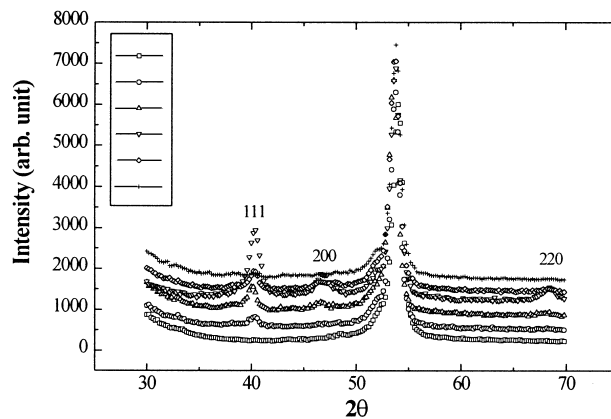


Fig. 4. Spectra of XRD on Pt-Ru catalysts prepared in chloroplatinic acid solution of various ruthenium chloride concentrations: (- \square -) BPG; (- \circ -) 5 mM; (- Δ -) 10 mM; (- ∇ -) 20 mM; (- \diamond -) 30 mM; (- + -) 40 mM.

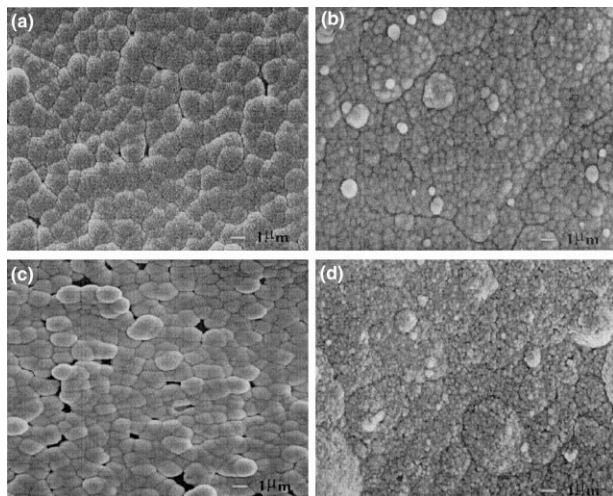


Fig. 5. SEM images of Pt–Ru catalysts prepared in chloroplatinic acid solution of ruthenium chloride concentrations (4:1, a,b) and (1:1, c,d): before methanol oxidation (a,c); after (b,d).

vs. atomic percent of ruthenium in the electrodeposition solution. Pt–Ru catalysts prepared in ruthenium chloride solutions of chloroplatinic acid (1:1) show better electrocatalytic activity than catalysts prepared in different concentrations of ruthenium chloride solution. The amount of methanol oxidised decreased as the amount of platinum present decreases because methanol is decomposed only on the platinum surface. Eventually, the total current for methanol oxidation decreases. Even though the amount of methanol oxidised is increased as the amount of platinum increases, the peak current decreases because all oxidation pathways for CO intermediates are possible. Contrarily, for 50% ruthenium contents, currents arise mainly due to Eq. (3) and contribute to the peak current more effectively than that for other ruthenium contents.

The growth of Pt–Ru catalysts was investigated by using XRD. Fig. 4 shows spectra of XRD on Pt–Ru catalysts prepared from chloroplatinic acid solution of various ruthenium chloride concentrations. Peaks located at 40.1, 46.3 and 68.6 (2θ) are attributed to 111, 200 and 220 faces, respectively [5,7,12]. The peak located at 40.1 (2θ) increases as the content of ruthenium increases, showing a maximum for 50% of ruthenium, and again decreasing at greater than 50%. This indicates that Pt–Ru catalysts prepared from a ruthenium chloride solution of chloroplatinic acid (1:1) deposit and grow more effectively than that under other electrodeposition conditions. From the above-results, it could be concluded that Pt–Ru catalysts prepared in chloroplatinic acid solutions of ruthenium chloride concentration (1:1) displayed the best catalytic activity.

Fig. 5 represents the SEM photography of the surface morphology for Pt–Ru catalysts before and after methanol oxidation (4:1, (a) before methanol oxidation, (b) after

methanol oxidation) and (1:1, (c) before, (d) after). As shown in the figure, there is no significant difference of surface morphology resulting from changing the $\text{RuCl}_3/\text{H}_2\text{PtCl}_6$ ratios. However, the aggregation of catalyst clusters appear after methanol oxidation. This could be due to the growth of the catalyst particle size during methanol oxidation in phosphoric acid solution.

4. Conclusions

The electrooxidation of methanol on Pt–Ru catalysts supported by basal plane graphite was investigated in phosphoric acid solution. Peak potentials for methanol oxidation are shifted to low potentials as the concentration ratio of Ru/Pt increases. The shift of peak potential is due to the different oxidation pathway of CO adsorbed on the Pt–Ru surface. For methanol oxidation in phosphoric acid and methanol solutions, the electrocatalytic activity of catalysts prepared in chloroplatinic acid solutions of ruthenium chloride concentration (1:1) was better than that of catalysts prepared in different concentrations of ruthenium chloride. Catalyst clusters were aggregated after methanol oxidation.

Acknowledgements

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